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(57) Abstract

Never-dried lyocell fibre may be treated with an aqueous liquor containing from 10 to 18 percent by weight sodium hydroxide for 20 seconds or more in order to provide a degree of control over fibrillation tendency and to increase the water imbibition, absorbency and/or dyeability of the fibre.

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FIBRE MANUFACTURE

Field of the invention

This invention relates to processes for the manufacture of lyocell fibre, in particular to processes wherein a solution of cellulose in an aqueous tertiary amine N-oxide solvent is extruded by way of a spinnerette through a gaseous gap into a coagulating bath to provide a fibre which is then washed and dried.

Background art

Lyocell fibres are known, and their manufacture is described for example in US-A-4,416,698, the contents of which are incorporated herein by way of reference. Cellulose is dissolved in a solvent containing a tertiary amine N-oxide (which may also be called for brevity an amine oxide), for example N-methylmorpholine N-oxide (NMMO). The solvent generally also contains a proportion of a non-solvent for cellulose, for example water. The resulting solution is extruded through a suitable die to produce fibres, which are coagulated, washed in water to remove the solvent, and dried. This process of extrusion and coagulation is referred to as "solvent-spinning", and the cellulose fibre produced thereby is referred to as "solvent-spun" cellulose fibre or as lyocell fibre. It is also known that cellulose fibres can be made by extrusion of a solution of a cellulose derivative into a regenerating and coagulating bath. One example of such a process is the viscose process, in which the cellulose derivative is cellulose xanthate. Solvent-spinning has a number of advantages over other known processes for the manufacture of elongate cellulose members such as the viscose process, for example reduced environmental emissions.

Lyocell fibres are known to be prone to fibrillation. Fibrillation is a phenomemon which in the main occurs when lyocell fibres are subjected to mechanical forces during wet-processing, and it results in the partial detachment of fine longitudinal fibrils from the fibres. Fibrillation is in general considered to be undesirable in textile end-uses,

and efforts have been made to reduce or eliminate fibrillation tendency by chemical aftertreatments, such as those described in US-A-5,310,424, or by suitable choice of spinning parameters, as described for example in WO-A-95/02082. However, at least some tendency to fibrillation is desirable in certain other processes and end-uses, for example paper-making and filtration. It is an object of the invention to provide a method of manufacturing lyocell fibres of controlled fibrillation tendency.

Disclosure of invention

According to the present invention there is provided a method for the manufacture of lyocell fibre, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;

(2) passing the elongate form through at least one water-containing bath to remove the organic solvent from the elongate form, thereby producing a reconstituted cellulosic fibre;

(3) as characterising step, applying to the reconstituted cellulosic fibre for 20 seconds or more an aqueous liquor which comprises from 10 to 18 percent by weight sodium hydroxide;

(4) washing the reconstituted cellulosic fibre to remove sodium hydroxide therefrom; and

(5) drying the reconstituted cellulosic fibre, thereby forming the lyocell fibre.

Any suitable dissolving-grade cellulose may be used to form the solution. The average degree of polymerisation (D.P.) of the cellulose is generally in the range from 250 to 2000, preferably from 500 to 1000. The concentration of cellulose in the solution is generally in the range from 5 to 25 percent by weight. The organic solvent is preferably an aqueous tertiary amine N-oxide, more preferably aqueous N-methylmorpholine N-oxide. Mixtures of tertiary amine N-oxides may be used. The solution may

also comprise one or more water-miscible non-solvents for cellulose in known manner. The solution preferably comprises from 5 to 20 percent by weight water. The solution may also comprise one or more dispersed substances, for example a pigment such as titanium dioxide, and/or one or more other dissolved substances, for example a stabiliser such as propyl gallate, in known manner. The temperature of the solution supplied to the die is preferably in the range from 80 to 120°C.

The solution is preferably extruded from the die into a water-containing coagulating bath by way of a gaseous gap. The gas in the gaseous gap is preferably air, although other inert gases or gas mixtures may also be used. The length of the gaseous gap (i.e. the distance between the face of the die and the surface of the coagulating bath) is preferably in the range from 10 to 100 mm, more preferably 20 to 40 mm. Gas is preferably supplied into and extracted from the gaseous gap generally transversely to the direction of travel of the elongate form therethrough, as described in WO-A-94/28218. The velocity of the supplied gas is preferably in the range from 1 to 10 m/s. The temperature of the supplied gas is preferably in the range from 0 to 30°C. The relative humidity of the supplied gas is preferably in the range from 0 to 60 percent. The absolute humidity of the supplied gas is preferably in the range from 0 to 20, more preferably from 6 to 15, g/kg.

The elongate form coagulates in the water-containing bath into which it is extruded so as to form a reconstituted cellulosic fibre. This bath preferably comprises from 0 to 70, more preferably from 20 to 40, percent by weight of the same tertiary amine N-oxide as the solution. The velocity of the fibre as it is removed from the coagulating bath is preferably in the range from 20 to 150 m/min.

The concentration of sodium hydroxide in the aqueous liquor of step (3) is preferably in the range from 10 to 13

percent by weight. The temperature of the aqueous liquor is preferably in the range from 10 to 70°C, more preferably from 10 to 40°C. The aqueous liquor may be applied to the fibre by any convenient means, for example from a circulating bath.

The time between application of the aqueous liquor to the fibre and washing to remove the sodium hydroxide therefrom is conveniently in the range from 20 to 120 seconds. The washing process may commence with application of an aqueous acid solution to the fibre and continues by washing with water until the pH of the fibre approaches neutrality. The acid may be a mineral acid such as hydrochloric acid or sulphuric acid, the concentration thereof in the aqueous acid solution being in the range from 0.1 to 20, more preferably from 1 to 15, percent by volume, or it may be an organic acid such as acetic acid, the concentration thereof in the aqueous acid solution being in the range from 25 to 75, more preferably from 40 to 60, percent by volume. The temperature of the aqueous acid solution may conveniently be around ambient temperature, for example in the range from 10 to 40°C. Higher temperatures are generally preferred at higher concentrations of sodium hydroxide; thus, preferred temperature ranges at 11, 12 and 13 percent by weight sodium hydroxide are 25 to 35, 30 to 35 and 30 to 40°C, respectively. We have found that such higher temperatures serve to assist rinsing but do not affect fibrillation tendency. The aqueous acid solution may be applied to the fibre by any convenient means, for example from a circulating bath. The residence time in such a bath may conveniently be in the range from 20 to 120 seconds. Good results can alternatively be obtained by washing the fibre with hot water alone, followed by a sour wash with dilute aqueous acid to bring fibre pH below 7.

The cellulosic fibre to which the aqueous liquor or the aqueous acid is or has been applied may be held in relaxed state or under tension. Alkaline treatment either in relaxed

state or under tension has surprisingly been observed to reduce fibrillation tendency, although the degree of reduction is generally greater when the treatment is performed on fibre in relaxed state. The method of the invention may be found to increase one or more of the water imbibition, the absorbency and the dyeability of the fibres. The method of the invention therefore permits some degree of control over fibre properties, including fibrillation tendency, in a simple manner.

Other operations may be performed on the reconstituted cellulosic fibre, such as the drying step (5) and optional operations such as bleaching and cutting to staple length, in known manner.

The method of the invention is applicable to fibre in the form of continuous filaments, tow or staple fibre. The titre of lyocell fibre produced by the method of the invention may be in the range from 0.5 to 10 dtex, often from 1 to 2.5 dtex.

Fibrillation tendency of lyocell fibres can be assessed by the following Test Method:-

Test Method 1 (Blender)

The Fibrillation Index (FI) of lyocell fibres may be assessed microscopically by comparison with a standard graded scale of lyocell fibres exhibiting various degrees of fibrillation, as described in EP-A-0,538,977 under Test Method 1.

Dry lyocell fibre (approx. 0.05 g) is cut to 10mm lengths and placed in an industrial blender together with 400 ml tap water. The blender is then operated for a time between 30 sec and 3 min to induce fibrillation; the time required depends inter alia on the nature of the blender blade and is chosen so that a standard sample of commercial

lyocell fibre (available from Courtaulds Fibres (Holdings) Limited under the Trade Mark TENCEL) exhibits FI in the range 6.5 to 8.0. The fibres are collected, and samples of them are placed on two microscope slides. Three sets of five comparisons with the standard graded scale are made on each slide, and the results are averaged to yield the FI of the sample.

The invention is illustrated by the following Examples, in which parts and proportions are by weight unless otherwise specified:-

Example 1

A solution of cellulose (15%) in NMMO (75%) and water (10%) was extruded through a spinnerette into an aqueous coagulating bath to produce 1.4 dtex filaments. After washing with water to remove NMMO, the filaments were treated in taut or relaxed state with aqueous NaOH for 30 seconds, washed in taut or relaxed state with aqueous acid for 30 seconds, rinsed and dried. Further experimental details and results are given in Table 1:

Table 1

Sample	NaOH %	Temp °C	Acid	Concn. % v/v	Temp °C	Tension	FI
1.1	11.5	14	AcOH	50	17	taut	5.7
1.2	11.5	24	AcOH	60	16	relaxed	2.5
1.3	11.5	35	AcOH	40	17	relaxed	5.0
1.4	11.5	15	HCl	10	19	taut	4.8
1.5	11.5	24	HCl	15	19	relaxed	2.4
1.6	11.5	35	HCl	5	17	relaxed	5.3
1.7	11.5	15	H_2SO_4	10	19	taut	3.7
1.8	11.5	25	H_2SO_4	15	22	relaxed	3.8
1.9	11.5	35	H_2SO_4	5	24	relaxed	4.0
1.10	11.5	15	H_2SO_4	0.4	17	taut	3.8
1.11	11.5	24	AcOH	60	16	relaxed	2.5
1.12	11.5	35	HCl	0.8	16	relaxed	2.5
1.13	11.5	15	AcOH	60	17.5	relaxed	5.1
1.14	11.5	15	HCl	15	17.5	relaxed	4.1
1.15	11.5	15	H_2SO_4	15	18	relaxed	4.4
1.16	11.5	15	AcOH	40	17	relaxed	3.9
1.17	11.5	15	HCl	5	17	relaxed	4.4
1.18	11.5	15	H_2SO_4	5	17.5	relaxed	5.8
1.19	11.5	35	AcOH	60	18	relaxed	4.4
1.20	11.5	35	HCl	15	20	relaxed	4.0
1.21	11.5	35	H_2SO_4	15	25	relaxed	3.9
1.22	11.5	25	AcOH	60	19	relaxed	3.1
1.23	11.5	25	HCl	15	19	relaxed	3.8
1.24	11.5	25	H_2SO_4	15	20.5	relaxed	2.6

(AcOH represents acetic acid).

Example 2

Example 1 was repeated, except that the strength of the aqueous NaOH was 11.5%, the aqueous acid was 15% v/v sulphuric acid, and the NaOH and acid treatments were performed on the fibre in taut, relaxed or stretched state. Further experimental details and results are given in Table 2:

Table 2

Sample	NaOH Temp °C	NaOH Tension	H_2SO_4 Temp °C	H_2SO_4 Tension	FI
2.1	20	relaxed	25	relaxed	3.0
2.2	19	relaxed	25	taut	3.4
2.3	20	relaxed	20	stretched	3.1
2.4	19.5	taut	25	relaxed	7.0
2.5	20	taut	26	stretched	3.9
2.6	19.5	taut	25	taut	2.9
2.7	20	stretched	25	relaxed	5.0
2.8	20	stretched	25	taut	4.9
2.9	19.5	stretched	25	stretched	6.2

Example 3

Example 1 was repeated, except that the fibre was treated for 30 sec with 11.5% NaOH at 25°C followed by washing at 25°C with various liquors. The Fibrillation Indexes (FIs) shown in Table 3 were obtained:

Table 3

	Water	0.5% v/v H_2SO_4	2% v/v H_2SO_4	5% v/v H_2SO_4	10% v/v H_2SO_4	15% v/v H_2SO_4
FI	2.6 & 2.0	3.0	2.1	1.6 & 2.3	1.4 & 1.5	2.4

In a further series of experiments, the fibre was treated for 30 sec with aqueous NaOH followed by washing with various liquors at 25°C or with hot water. The Fibrillation Indexes (FIs) shown in Table 4 were obtained:

Table 4

NaOH %	NaOH °C	Water	Hot Water	5% v/v H_2SO_4	10% v/v H_2SO_4	15% v/v H_2SO_4
11	10	long fibrils broken off		fibre totally destroyed		
11	20	2.6	1.8	long fibrils broken off		2.9
11	30	3.3	1.8	2.0	2.0	2.5
13	20	4.3	2.4	2.0	2.1	2.8

Treatment at 10°C or at 20°C followed by washing with 5 or 10% v/v H_2SO_4 resulted in excessive fibre damage. FI was not measured on the samples marked "long fibrils broken off" because it is believed that such FIs would be misleading.

CLAIMS

1. A method for the manufacture of lyocell fibre, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;

(2) passing the elongate form through at least one water-containing bath to remove the organic solvent therefrom, thereby producing a reconstituted cellulosic fibre;

(3) as characterising step, applying to the reconstituted cellulosic fibre for 20 seconds or more an aqueous liquor which comprises from 10 to 18 percent by weight sodium hydroxide;

(4) washing the reconstituted cellulosic fibre to remove sodium hydroxide therefrom; and

(5) drying the reconstituted cellulosic fibre, thereby forming the lyocell fibre.

2. A method according to claim 1, further characterised in that the aqueous liquor of application step (3) contains from 10 to 13 percent by weight sodium hydroxide.

3. A method according to claim 1 or claim 2, further characterised in that the temperature of the aqueous liquor of application step (3) is in the range from 10 to 70°C, preferably from 10 to 40°C.

4. A method according to any one of the preceding claims, further characterised in that the time between application of the aqueous liquor in step (3) and washing in step (4) is in the range from 20 to 120 seconds.

5. A method according to any one of the preceding claims, further characterised in that the washing step (4) involves washing the fibre with an aqueous solution

containing from 0.1 to 20, preferably from 1 to 15, percent by volume of an acid selected from the group consisting of hydrochloric acid and sulphuric acid.

6. A method according to any one of claims 1 to 4, further characterised in that the washing step (4) involves washing the fibre with an aqueous solution containing from 25 to 75, preferably from 40 to 60, percent by volume acetic acid.

7. A method according to claim 5 or claim 6, further characterised in that the temeperature of the aqueous acid solution used in step (4) is in the range from 10 to 40°C.

8. A method according to any one of claims 1 to 4, further characterised in that the washing step (4) involves washing the fibre firstly with hot water and secondly with dilute aqueous acid thereby bringing the pH of the fibre below 7.

9. A method according to any one of the preceding claims, further characterised in that throughout application step (3) the fibre is maintained in relaxed state.

10. A method according to any one of claims 1 to 8, further characterised in that the fibre to which the aqueous liquor of application step (3) is or has been applied is held under tension prior to introduction into the washing step (4).

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D01F C08J D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 24524 A (COURTAULDS FIBRES HOLDINGS LTD ;TAYLOR JAMES MARTIN (GB)) 14 September 1995 see the whole document ---	
A	WO 95 28516 A (COURTAULDS FIBRES HOLDINGS LTD ;POTTER CHRISTOPHER DAVID (GB); DOB) 26 October 1995 see the whole document ---	
A	WO 92 14871 A (COURTAULDS PLC) 3 September 1992 see the whole document -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. ial Application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9524524 A	14-09-95	AU 1854295 A	25-09-95
		CA 2184391 A	14-09-95
		CN 1143397 A	19-02-97
		CZ 9602555 A	12-02-97
		EP 0749505 A	27-12-96
		FI 963484 A	05-09-96
		PL 316176 A	23-12-96
		SK 112696 A	09-04-97
		ZA 9501842 A	12-12-95
WO 9528516 A	26-10-95	AU 2219295 A	10-11-95
		CN 1146223 A	26-03-97
		CZ 9603015 A	12-02-97
		EP 0755467 A	29-01-97
		FI 964127 A	14-10-96
		NO 964361 A	14-10-96
		SK 117196 A	05-03-97
WO 9214871 A	03-09-92	AU 1241092 A	15-09-92
		BR 9205616 A	02-08-94
		CZ 9301582 A	16-02-94
		EP 0571460 A	01-12-93
		JP 6505060 T	09-06-94
		SK 85093 A	12-01-94
		US 5403530 A	04-04-95